

TITANIUM DIOXIDE BASED HYBRID PHOTOCATALYST  
FOR SEAWATER DESALINATION PRE-TREATMENT

WEERANA A/P EH KAN

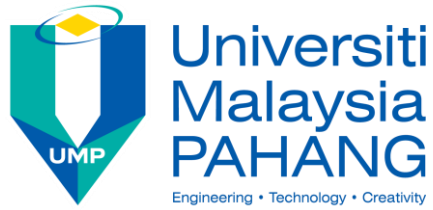
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UNIVERSITI MALAYSIA PAHANG



## **SUPERVISOR'S DECLARATION**

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## **STUDENT'S DECLARATION**

I hereby declare that the work in this thesis is my own except for the quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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for the award of the degree of  
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Special dedication of grateful and blissful feeling to my:

Beloved late father;

Mr. Eh Kan

Beloved mother;

Mrs. Suni

Loving older brother and younger sister;

Withun and Wemalai

And all of my caring friends

For their continuous love, support, encouragement and best wishes

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## LIST OF SYMBOLS

<i>nm</i>	Nanometer
$^{\circ}\text{C}$	Degree Celsius
<i>eV</i>	Electron volt
$\lambda$	Wavelength
<i>h\nu</i>	Light energy
<i>mg/L</i>	Milligram per liter
<i>mS/cm</i>	Milli siemens per centimetre
<i>NTU</i>	Nephelometric turbidity units
<i>ppt</i>	Part per trillion
<i>g/L</i>	Gram per liter
<i>TCU</i>	True colour units
$\mu\text{S/cm}$	Micro siemens per centimeter
$\mu\text{m}$	Micro meter
$\theta$	Theta
<i>W</i>	Watt
<i>V</i>	Volt
<i>ppm</i>	Part per million
<i>rpm</i>	Revolutions per minute
<i>Mol%</i>	Molar percent
<i>wt%</i>	Weight percent
<i>hrs</i>	Hours



## LIST OF ABBREVIATIONS

AN	Ammoniacal nitrogen
AOP	Advanced oxidation processes
BET	Brunauer Emmett Teller
BOD	Biochemical oxygen demand
ED	Electrodialysis
Cb	Conduction band
CHNS	Carbon, hydrogen, nitrogen, sulphur
COD	Chemical oxygen demand
CVD	Chemical vapour deposition
DO	Dissolved oxygen
DOE	Department of Environment
EDI	Electrodeionization
EU	European Union
FF	Fiber filter
GC-TCD	Gas chromatography with thermal conductivity detector
HR	High range
ID	Diameter
INWQS	Interim National Water Quality Standards for Malaysia
K	Kubelka-Munk
pH	Potential hydrogen
MED	Multi-effect distillation
MO	Methyl orange
MSF	Multi-stage flash distillation

PEC	Photoelectrochemical
RO	Reverse osmosis
OPFA	Oil palm fiber ash
SEM	Scanning electron microscopy
SS	Suspended solids
SWRO	Seawater reverse osmosis
TDS	Total dissolved solid
UNICEF	United Nations International Children's Emergency Fund
UV	Ultraviolet
UV/Vis/Nir	Ultraviolet visible near-UV and near-infrared
Vb	Valence band
WHO	World Health Organization
WQI	Water quality index
XRD	X-ray diffraction
XRF	X-ray fluorescence

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## ABSTRACT

The application of hybrid titanium dioxide ( $\text{TiO}_2$ ) photocatalyst in treating water resources has huge economic potential and an attractive alternative technology for seawater pre-desalination. The objective of this investigation is to study the effectiveness of photocatalytic reactor system via hybrid photocatalyst that content oil palm fiber ash (OPFA),  $\text{TiO}_2$  and metal promoter in the seawater desalination pre-treatment. The study was carried out in a one liter borosilicate photoreactor for 1 hr to 4 hrs. The catalyst to seawater sample weight ratio was varied from 1:300 to 1:500. The experiment was carried out by using mercury light (UV light) and halogen light (visible light). The chemical oxygen demand (COD), pH, dissolved oxygen (DO), turbidity, total dissolved solid (TDS) and conductivity of the seawater were analyzed prior and after the treatment. The fresh and spent catalysts were characterized via X-ray diffraction (XRD), scanning electron microscopy (SEM),  $\text{N}_2$  adsorption, ultraviolet visible near-UV/near-infrared (UV/Vis/Nir), elemental analysis (carbon, hydrogen, nitrogen and sulphur (CHNS)) and X-ray fluorescence (XRF). The gas product was analyzed by using gas chromatography with thermal conductivity detector (GC-TCD). The  $\text{TiO}_2$  catalyst can reduce salt concentration for more than 7 % and decrease up to 8 % of COD. The OPFA was able to adsorb about 3 % of salt in either with the present or absent of lights. Furthermore, OPFA reduced seawater COD for more than 10 % the light presence and 4 % in without light present. The hybrid catalyst containing  $\text{TiO}_2$ :Ash 50:50 was calcined at 500 °C, reduced more than 9 % of salt and 24 % of COD reduction in the seawater. It is found that the  $\text{TiO}_2$ :Ash 50:50 catalyst has dual functions, ie. the catalyst was able to adsorb the salt and decompose the water contaminants resulting in lower conductivity and COD in the seawater. However, the hybrid  $\text{TiO}_2$ :Ash 50:50 catalyst which calcined at 800 °C was only able to reduce 2 % of salt and 14 % of COD reduction in the seawater. Better  $\text{TiO}_2$ :Ash 50:50 catalyst reactivity was achieved when UV light was used than visible light. Higher water temperature was observed when visible light was applied that leads to distillation dominating the process. The optimum parameters for photocatalytic reaction was obtained by using hybrid  $\text{TiO}_2$ :Ash 50:50 catalyst when catalyst to water weight ratio was at 1:400 and operating for 2 hrs. Iron (Fe) and nickel (Ni) can be loaded into the catalyst. Fe loading in the catalyst was found to perform better than Ni. The best condition was obtained when visible light and  $\text{TiO}_2$ :Ash:Fe 47.5:47.5:5 were used. The  $\text{TiO}_2$ :Ash:Fe 47.5:47.5:5 reduced 16 % and 22 % of salt concentration and COD respectively. While, the  $\text{TiO}_2$ :Ash:Ni 47.5:47.5:5 was only able to reduce up to 13 % of salt in the seawater and decrease 22 % of seawater COD at the same condition. In conclusion, better water quality can be achieved via photocatalytic reaction by using hybrid photocatalyst. Thus, the photocatalysis process is able to provide an effective alternative pre-treatment for seawater desalination.

## ABSTRAK

Aplikasi fotomangkin hibrid titanium dioksida ( $\text{TiO}_2$ ) dalam merawat sumber air mempunyai potensi yang tinggi dalam ekonomi dan menjadi teknologi alternatif untuk penyahgaraman air laut. Tujuan penyiasatan ini adalah untuk mengkaji keberkesanan sistem reaktor fotopemangkin melalui tindak balas mangkin yang mengandungi abu serat kelapa sawit (OPFA),  $\text{TiO}_2$  dan penambahan logam dalam rawatan awal penyahgaraman air laut. Kajian ini telah dijalankan dalam fotoreaktor selama satu jam sehingga empat jam. Nisbah mangkin kepada sampel air laut telah dikaji iaitu nisbah 1:400 sehingga 1:500. Cahaya merkuri (cahaya ungu) ultraungu dan cahaya halogen (tampak) telah digunakan. Permintaan oksigen kimia (COD), pH, oksigen terlarut (DO), kekeruhan, jumlah pepejal terlarut (TDS) dan konduktiviti air laut telah dianalisis sebelum dan selepas ujian. Mangkin sebelum dan selepas digunakan disifatkan melalui sinar pembelauan (XRD), imbasan mikroskop elektron (SEM), penjerapan  $\text{N}_2$ , ultraviolet kelihatan hampir UV/hampir infrared (UV/Vis/Nir), analisis unsur (karbon, hidrogen, nitrogen dan sulfur (CHNS)) dan sinar pendarfluor (XRF). Produk gas dianalisis dengan menggunakan kromatografi gas dengan pengesan kekonduksian haba (GC-TCD). Pemangkin  $\text{TiO}_2$  berjaya mengurangkan kepekatan garam dan COD masing-masing lebih daripada 7 % and 8 %. Manakala OPFA dapat menjerap sekurang-kurangnya 3 % garam sama ada dengan kehadiran cahaya dan sebaliknya. Seterusnya, OPFA mengurangkan lebih daripada 10 % COD dengan kehadiran lampu dan 4 % dengan tanpa kehadiran lampu. Mangkin hibrid yang mengandungi  $\text{TiO}_2$ :Ash peratusan nisbah berat 50:50 yang dikalsinasi pada  $500\text{ }^\circ\text{C}$  telah berjaya mengurangkan lebih daripada 9 % komponen garam and 24 % pengurangan COD air laut. Ia telah didapati bahawa mangkin  $\text{TiO}_2$  mempunyai dua fungsi, i.e. mangkin berupaya dalam menjerap garam dan mengurai bahan air tercemar menyebabkan kekonduksian dan COD yang lebih rendah di dalam air laut. Walaubagaimanapun, mangkin hibrid yang mengandungi  $\text{TiO}_2$ :Ash 50:50 yang dikalsinasikan pada  $800\text{ }^\circ\text{C}$  berupaya mengurangkan kepekatan garam sebanyak 2 % dan COD sebanyak 14 % di dalam sampel air laut. Kereaktifan mangkin hibrid  $\text{TiO}_2$  yang baik dicapai apabila menggunakan lampu yang bergelombang cahaya ultraungu berbanding cahaya tampak. Suhu air yang lebih tinggi diperolehi apabila menggunakan lampu bergelombang cahaya tampak yang menyebabkan penyulingan mendominasi proses. Parameter optimal untuk tindak balas fotopemangkin diperolehi dengan menggunakan mangkin hibrid  $\text{TiO}_2$ :Ash 50:50 apabila nisbah berat mangkin kepada air pada 1:400 dan beroperasi selama dua jam. Ferum (Fe) dan nikel (Ni) boleh ditambahkan di dalam mangkin. Penambahan logam Fe menghasilkan mangkin yang lebih baik daripada Ni. Mangkin  $\text{TiO}_2$ :Ash:Fe 47.5:47.5:5 didapati mempunyai reaktiviti terbaik menggunakan lampu bergelombang cahaya tampak. Mangkin  $\text{TiO}_2$ :Ash:Fe 47.5:47.5:5 berjaya mengurangkan kepekatan garam lebih daripada 16 % dan 22 % COD. Manakala,  $\text{TiO}_2$ :Ash:Ni 47.5:47.5:5 hanya dapat menurunkan kepekatan garam air laut kepada 13 % dan 22 % COD dalam keadaan yang sama. Kesimpulannya, kualiti air yang lebih baik boleh dicapai melalui tindak balas fotopemangkin dengan menggunakan mangkin hibrid. Oleh itu, proses fotopemangkin ini boleh menyediakan alternatif rawatan awal yang berkesan untuk penyahgaraman air laut.

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